PATENT ABSTRACTS OF JAPAN

(11)Publication number : 11-329444
(43)Date of publication of application : 30.11.1999

(51)Int.CI. H01M 4/62
H01M 4/02
H01M 10/40

(21)Application number : 10-138985
(22)Date of filing : 20.05.1998

(71)Applicant : SHIN KOBE ELECTRIC MACH CO LTD
(72)Inventor : HARA KENJI
MAEJIMA TOSHIKAZU
TANAKA NOBUKAZU

(54) NONAQUEOUS ELECTROLYTE SECONDARY BATTERY

(57)Abstract:
PROBLEM TO BE SOLVED: To improve a high-temperature life characteristic by using a composite oxide containing lithium and manganese as positive electrode active material, and including any one of ammonium phosphate, ammonium phosphate compound, ammonium polyphosphate, and ammonium polyphosphate compound.
SOLUTION: When ammonium polyphosphate is added to a positive electrode, lithium manganese having an average particle size of 10 μm, carbon powder having an average particles size of 3 μm and vinylidene polyfluoride as binder are dispersed in N-methyl-pyrolidene as solvent and mixed to prepare a slurry. Ammonium polyphosphate is added to the prepared slurry followed by kneading again to form a slurry solution. This slurry is applied to both sides of an aluminum foil 20 μm thick as a current collector, dried, and then integrated by pressing. Thereafter, it is cut to a piece 54 mm in width and 450 mm in length to form a strap shape positive electrode.

LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]
[Date of extinction of right]

(19)日本国特許庁（ＪＰ）　(12)公開特許公報（Ａ）　(11)特許出願公開番号

特開平11－329444

(43)公開日　平成11年(1999)11月30日

(51)Int.Cl.⁶		識別記号	ＰＩ		
Ｈ０１Ｍ	4/62		Ｈ０１Ｍ	4/62	Ｚ
	4/02			4/02	Ｃ
					Ｄ
	10/40			10/40	Ｚ

審査請求　未請求　請求項の数１　ＯＬ　（全３頁）

(21)出願番号　特願平10－139985

(22)出願日　平成10年(1998)５月20日

(71)出願人　000001203
新神戸電機株式会社
東京都中央区日本橋本町２丁目８番７号

(72)発明者　原　賢二
東京都中央区日本橋本町２丁目８番７号
新神戸電機株式会社内

(72)発明者　前島　敏和
東京都中央区日本橋本町２丁目８番７号
新神戸電機株式会社内

(72)発明者　田中　伸和
東京都中央区日本橋本町２丁目８番７号
新神戸電機株式会社内

(54)【発明の名称】　非水電解液二次電池

(57)【要約】
【課題】リチウムとマンガンを含む複合酸化物を正極活物質とする非水電解液二次電池の高温寿命特性を向上させる。
【解決手段】正極または負極に、リン酸アンモニウム、リン酸アンモニウム化合物、ポリリン酸アンモニウムまたはポリリン酸アンモニウム化合物のうちのいずれかを含有させる。

1

【特許請求の範囲】

【請求項１】リチウムとマンガンを含む複合酸化物を正極活物質とする非水電解液二次電池であって、正極または負極に、リン酸アンモニウム、リン酸アンモニウム化合物、ポリリン酸アンモニウムまたはポリリン酸アンモニウム化合物のうちのいずれかを含有させたことを特徴とする非水電解液二次電池。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は、リチウムとマンガンを含む複合酸化物を正極活物質とする非水電解液二次電池に関するものである。

【０００２】

【従来の技術】従来、マンガン酸リチウム等のようなリチウムとマンガンを含む複合酸化物を正極活物質とする非水電解液二次電池の場合には、例えば５０℃の高温時に正極の活物質からマンガンが溶出し、このマンガンイオンが電解液を通じて負極に到り負極に析出して容量劣化を起こすため、サイクル寿命性能が損なわれていた。

【０００３】

【発明が解決しようとする課題】本発明は、前記問題点に鑑みてなされたものであって、リチウムとマンガンを含む複合酸化物を正極活物質とする非水電解液二次電池における高温寿命特性を向上させることを目的とする。

【０００４】

【課題を解決するための手段】本発明は上記課題を解決するためになされたもので、リチウムとマンガンを含む複合酸化物を正極活物質とする非水電解液二次電池であって、正極または負極に、リン酸アンモニウム、リン酸アンモニウム化合物、ポリリン酸アンモニウムまたはポリリン酸アンモニウム化合物のうちのいずれかを含有させたことを特徴とするものである。

【０００５】

【発明の実施の形態】以下に本発明の実施の形態について例をあげて説明する。

１．正極にポリリン酸アンモニウムを添加

平均粒径が１０μｍのマンガン酸リチウム、平均粒径が３μｍの炭素粉末と、結着剤としてポリフッ化ビニリデン（商品名：ＫＦ＃１２０、呉羽化学工業（株）製）とを、溶媒であるＮ－メチル－２－ピロリドンに分散させて混合してスラリーを作製する。本発明では、作製したスラリーにポリリン酸アンモニウムを添加した後に再び混練し、スラリー状の溶液にした。このスラリーを集電体である厚みが２０μｍのアルミニウム箔の両面に塗布、乾燥後、プレスして一体化する。その後、幅が５４ｍｍ、長さが４５０ｍｍに切断して短冊状の正極を作製した。

【０００６】２．負極にポリリン酸アンモニウムを添加

平均粒径が２０μｍの炭素粒子と、結着剤としてポリフッ化ビニリデン（商品名：ＫＦ＃１２０、呉羽化学工業

2

（株）製）とを溶媒であるＮ－メチル－２－ピロリドンに投入し混合して、スラリー状の溶液を作製する。本発明では、作製したスラリーにポリリン酸アンモニウムを添加した後に再び混練し、スラリー状の溶液にした。このスラリーを集電体である厚みが１０μｍの銅箔の両面に塗布、乾燥後、プレスして一体化する。その後、幅が５６ｍｍ、長さが５００ｍｍに切断して短冊状の負極を作製した。

【０００７】３．電池の組立て及び試験

作製した正極と負極とを組み合わせ、厚さが２５μｍ、幅が５８ｍｍのポリエチレン多孔膜からなるセパレータを介して捲回し、捲回群を作製する。正極、負極の組み合わせを表１に示す。この捲回群を電池缶に挿入し、電解液を５ｍｌ注液する。次に上蓋をつけた後かしめて密閉し、直径が１８ｍｍで高さが６５ｍｍの円筒型電池を作製した。作製した非水電解液二次電池は、電流値１ＣｍＡで初充電した。その後、５０℃の恒温槽内で電流値１ＣｍＡでの放電（放電終止電圧２．７ｖ）と電流値０．５ＣｍＡでの充電（充電終止電圧４．２ｖ、４時間）を繰り返す高温寿命試験を実施した。高温寿命サイクル数は、充放電サイクルを繰返し初期容量の８０％の容量まで下がったときのサイクル数で表した。

【０００８】

【実施例】本発明の実施例および比較例の電池を以下のように作成し、これらについて高温寿命試験をした結果を表１に示す。

（実施例１～５）ポリリン酸アンモニウム添加の影響

前記した条件で正極用スラリー中または負極用スラリー中に含まれる活物質重量として１００重量部に対し、ポリリン酸アンモニウムを１重量部または１０重量部を添加した。

【０００９】（比較例１）ポリリン酸アンモニウムを正極用スラリー及び負極用スラリー添加しないものを比較例１とした。

【００１０】表１より明らかなように、ポリリン酸アンモニウムを添加した実施例１～５は比較例１に比べて２～４倍の高温寿命をもつ優れた特性を示している。

【００１１】

【表１】

試料	ポリリン酸アンモニウム添加量（wt．％）		高温寿命サイクル数
	正極	負極	
比較例１	なし	なし	50
実施例１	1．0	なし	110
実施例２	10．0	なし	110
実施例３	なし	1．0	170
実施例４	なし	10．0	170
実施例５	1．0	1．0	200

【００１２】実施例１～５では、ポリリン酸アンモニウムをスラリー中に添加する方法を示したが、ポリリン酸アンモニウムをマンガン酸リチウム．炭素粉末又は結着剤と混合して用いたり、溶媒であるＮ－メチル－２－ピロリドンに投入して用いることも可能である。また、実施例では、ポリリン酸アンモニウムを用いたが．そのほかにリン酸アンモニウム．第３リン酸アンモニウム、リン酸二水素アンモニウムなど、他のリン酸アンモニウム化合物やリン酸アンモニウム複合化合物についても同様の効果を得ることができた。

【００１３】

【発明の効果】上述したように、本発明に係る非水電解液二次電池は．リチウムとマンガンを含む複合酸化物を正極活物質とするものであり、正極または負極に．リン酸アンモニウム．リン酸アンモニウム化合物、ポリリン酸アンモニウムまたはポリリン酸アンモニウム化合物のうちのいずれかを含有させたことにより、高温時におけるマンガンイオンの正極からの溶出または負極への析出を抑制して高温寿命特性を大幅に改善することができる。

* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]
[Claim 1] The nonaqueous electrolyte rechargeable battery which is a nonaqueous electrolyte rechargeable battery which uses the multiple oxide containing a lithium and manganese as positive active material, and is characterized by making a positive electrode or a negative electrode contain ammonium phosphate, an ammonium phosphate compound, ammonium polyphosphate, or the polyphosphoric acid ammonium compounds.

[Translation done.]

* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the nonaqueous electrolyte rechargeable battery which uses the multiple oxide containing a lithium and manganese as positive active material.
[0002]
[Description of the Prior Art] In order to elute manganese from the active material of a positive electrode at the time of a 50-degree C elevated temperature, and for this manganese ion to result in a negative electrode through the electrolytic solution, to deposit in a negative electrode and to cause capacity degradation conventionally in the case of the nonaqueous electrolyte rechargeable battery which uses the multiple oxide containing a lithium and manganese, such as a manganic acid lithium, as positive active material, the cycle-life engine performance was spoiled.
[0003]
[Problem(s) to be Solved by the Invention] This invention is made in view of said trouble, and aims at raising the elevated-temperature life property in the nonaqueous electrolyte rechargeable battery which uses the multiple oxide containing a lithium and manganese as positive active material.
[0004]
[Means for Solving the Problem] It is the nonaqueous electrolyte rechargeable battery which uses as positive active material the multiple oxide which was made in order that this invention might solve the above-mentioned technical problem, and contains a lithium and manganese, and is characterized by making a positive electrode or a negative electrode contain ammonium phosphate, an ammonium phosphate compound, ammonium polyphosphate, or the polyphosphoric acid ammonium compounds.
[0005]
[Embodiment of the Invention] An example is given and explained about the gestalt of operation of this invention below.
1. To a positive electrode, make it distribute at the N-methyl-2-pyrrolidone which is a solvent about polyvinylidene fluoride (trade name: KF#120, Kureha Chemical Industry Co., Ltd. make), mix ammonium polyphosphate with the manganic acid lithium whose addition mean diameter is 10 micrometers, and the carbon powder whose mean diameter is 3 micrometers as a binder, and produce a slurry. In this invention, after adding ammonium polyphosphate to the produced slurry, it kneaded again, and it was made the slurry-like solution. This slurry is pressed in both sides of aluminium foil whose thickness which is a charge collector is 20 micrometers after spreading and desiccation, and it unifies. Then, width of face cut to 54mm, die length cut to 450mm, and the strip-of-paper-like positive electrode was produced.
[0006] 2. With the carbon particle whose addition mean diameter is 20 micrometers about ammonium polyphosphate at a negative electrode, as a binder, supply at the N-methyl-2-pyrrolidone which is a solvent about polyvinylidene fluoride (trade name: KF#120, Kureha Chemical Industry Co., Ltd. make), mix, and produce a slurry-like solution. In this invention, after adding ammonium polyphosphate to the produced slurry, it kneaded again, and it was made the slurry-like solution. This slurry is pressed in both

sides of copper foil whose thickness which is a charge collector is 10 micrometers after spreading and desiccation, and it unifies. Then, width of face cut to 56mm, die length cut to 500mm, and the strip-of-paper-like negative electrode was produced.
[0007] 3. Combine an assembly, and the positive electrode and negative electrode of a cell which carried out test production, wind through the separator which consists of polyethylene porous membrane whose thickness is 25 micrometers, and whose width of face is 58mm, and produce a winding group. The combination of a positive electrode and a negative electrode is shown in a table 1. This winding group is inserted in a cell can, and 5ml of electrolytic solutions is poured in. Next, after attaching a top cover, it sealed in total, and the diameter produced the cylindrical cell whose height is 65mm by 18mm. The produced nonaqueous electrolyte rechargeable battery charged initially by current value 1CmA. Then, elevated-temperature life test which repeats the discharge (discharge-final-voltage 2.7v) by current value 1CmA and the charge (charge termination electrical-potential-difference 4.2v, 4 hours) by current value 0.5CmA within a 50-degree C thermostat was carried out. The number of elevated-temperature life cycles was expressed with the number of cycles when repeating a charge-and-discharge cycle and falling to 80% of capacity of initial capacity.
[0008]
[Example] The cell of the example of this invention and the example of a comparison is created as follows, and the result of having carried out elevated-temperature life test about these is shown in a table 1.
(Examples 1-5) One weight section or 10 weight sections were added for ammonium polyphosphate to the 100 weight sections as active material weight contained in the slurry for positive electrodes, or the slurry for negative electrodes on the conditions in which ammonium polyphosphate addition carried out the effect above.
[0009] (Example 1 of a comparison) The slurry for positive electrodes and the thing which does not carry out slurry addition for negative electrodes were made into the example 1 of a comparison for ammonium polyphosphate.
[0010] The examples 1-5 which added ammonium polyphosphate show the outstanding property which has a 2 to 4 times as many elevated-temperature life as this compared with the example 1 of a comparison so that more clearly than a table 1.
[0011]
[A table 1]

試料	ポリリン酸アンモニウム添加量（wt．%）		高温寿命．サイクル数
	正 極	負 極	
比較例1	な し	な し	50
実施例1	1．0	な し	110
実施例2	10．0	な し	110
実施例3	な し	1．0	170
実施例4	な し	10．0	170
実施例5	1．0	1．0	200

[0012] Although examples 1-5 showed how to add ammonium polyphosphate in a slurry, it is also possible to supply and use ammonium polyphosphate for the N-methyl-2-pyrrolidone which mix with a manganic acid lithium, carbon powder, or a binder, and it uses, or is a solvent. Moreover, in the example, although ammonium polyphosphate was used, ammonium phosphate, the 3rd ammonium phosphate, ammonium dihydrogenphosphate, etc. were able to acquire the effectiveness same about other ammonium phosphate compounds and ammonium phosphate conjugated compounds.
[0013]
[Effect of the Invention] As mentioned above, by using the multiple oxide containing a lithium and

manganese as positive active material, and having made the positive electrode or the negative electrode contain ammonium phosphate, an ammonium phosphate compound, ammonium polyphosphate, or the polyphosphoric acid ammonium compounds, the nonaqueous electrolyte rechargeable battery concerning this invention can control the elution from the positive electrode of the manganese ion at the time of an elevated temperature, or the deposit to a negative electrode, and can improve an elevated-temperature life property substantially.

[Translation done.]

* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

TECHNICAL FIELD

[Field of the Invention] This invention relates to the nonaqueous electrolyte rechargeable battery which uses the multiple oxide containing a lithium and manganese as positive active material.

[Translation done.]

* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

PRIOR ART

[Description of the Prior Art] In order to elute manganese from the active material of a positive electrode at the time of a 50-degree C elevated temperature, and for this manganese ion to result in a negative electrode through the electrolytic solution, to deposit in a negative electrode and to cause capacity degradation conventionally in the case of the nonaqueous electrolyte rechargeable battery which uses the multiple oxide containing a lithium and manganese, such as a manganic acid lithium, as positive active material, the cycle-life engine performance was spoiled.

[Translation done.]

* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

EFFECT OF THE INVENTION

[Effect of the Invention] As mentioned above, by using the multiple oxide containing a lithium and manganese as positive active material, and having made the positive electrode or the negative electrode contain ammonium phosphate, an ammonium phosphate compound, ammonium polyphosphate, or the polyphosphoric acid ammonium compounds, the nonaqueous electrolyte rechargeable battery concerning this invention can control the elution from the positive electrode of the manganese ion at the time of an elevated temperature, or the deposit to a negative electrode, and can improve an elevated-temperature life property substantially.

[Translation done.]

* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] This invention is made in view of said trouble, and aims at raising the elevated-temperature life property in the nonaqueous electrolyte rechargeable battery which uses the multiple oxide containing a lithium and manganese as positive active material.

[Translation done.]

* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

MEANS

[Means for Solving the Problem] It is the nonaqueous electrolyte rechargeable battery which uses as positive active material the multiple oxide which was made in order that this invention might solve the above-mentioned technical problem, and contains a lithium and manganese, and is characterized by making a positive electrode or a negative electrode contain ammonium phosphate, an ammonium phosphate compound, ammonium polyphosphate, or the polyphosphoric acid ammonium compounds.
[0005]
[Embodiment of the Invention] An example is given and explained about the gestalt of operation of this invention below.
1. To a positive electrode, make it distribute at the N-methyl-2-pyrrolidone which is a solvent about polyvinylidene fluoride (trade name: KF#120, Kureha Chemical Industry Co., Ltd. make), mix ammonium polyphosphate with the manganic acid lithium whose addition mean diameter is 10 micrometers, and the carbon powder whose mean diameter is 3 micrometers as a binder, and produce a slurry. In this invention, after adding ammonium polyphosphate to the produced slurry, it kneaded again, and it was made the slurry-like solution. This slurry is pressed in both sides of aluminium foil whose thickness which is a charge collector is 20 micrometers after spreading and desiccation, and it unifies. Then, width of face cut to 54mm, die length cut to 450mm, and the strip-of-paper-like positive electrode was produced.
[0006] 2. With the carbon particle whose addition mean diameter is 20 micrometers about ammonium polyphosphate at a negative electrode, as a binder, supply at the N-methyl-2-pyrrolidone which is a solvent about polyvinylidene fluoride (trade name: KF#120, Kureha Chemical Industry Co., Ltd. make), mix, and produce a slurry-like solution. In this invention, after adding ammonium polyphosphate to the produced slurry, it kneaded again, and it was made the slurry-like solution. This slurry is pressed in both sides of copper foil whose thickness which is a charge collector is 10 micrometers after spreading and desiccation, and it unifies. Then, width of face cut to 56mm, die length cut to 500mm, and the strip-of-paper-like negative electrode was produced.
[0007] 3. Combine an assembly, and the positive electrode and negative electrode of a cell which carried out test production, wind through the separator which consists of polyethylene porous membrane whose thickness is 25 micrometers, and whose width of face is 58mm, and produce a winding group. The combination of a positive electrode and a negative electrode is shown in a table 1. This winding group is inserted in a cell can, and 5ml of electrolytic solutions is poured in. Next, after attaching a top cover, it sealed in total, and the diameter produced the cylindrical cell whose height is 65mm by 18mm. The produced nonaqueous electrolyte rechargeable battery charged initially by current value 1CmA. Then, elevated-temperature life test which repeats the discharge (discharge-final-voltage 2.7v) by current value 1CmA and the charge (charge termination electrical-potential-difference 4.2v, 4 hours) by current value 0.5CmA within a 50-degree C thermostat was carried out. The number of elevated-temperature life cycles was expressed with the number of cycles when repeating a charge-and-discharge cycle and falling to 80% of capacity of initial capacity.

[Translation done.]

EXAMPLE

[Example] The cell of the example of this invention and the example of a comparison is created as follows, and the result of having carried out elevated-temperature life test about these is shown in a table 1.
(Examples 1-5) One weight section or 10 weight sections were added for ammonium polyphosphate to the 100 weight sections as active material weight contained in the slurry for positive electrodes, or the slurry for negative electrodes on the conditions in which ammonium polyphosphate addition carried out the effect above.
[0009] (Example 1 of a comparison) The slurry for positive electrodes and the thing which does not carry out slurry addition for negative electrodes were made into the example 1 of a comparison for ammonium polyphosphate.
[0010] The examples 1-5 which added ammonium polyphosphate show the outstanding property which has a 2 to 4 times as many elevated-temperature life as this compared with the example 1 of a comparison so that more clearly than a table 1.
[0011]
[A table 1]

試料	ポリリン酸アンモニウム添加量（wt．%）		高温寿命サイクル数
	正 極	負 極	
比較例1	な し	な し	50
実施例1	1．0	な し	110
実施例2	10．0	な し	110
実施例3	な し	1．0	170
実施例4	な し	10．0	170
実施例5	1．0	1．0	200

[0012] Although examples 1-5 showed how to add ammonium polyphosphate in a slurry, it is also possible to supply and use ammonium polyphosphate for the N-methyl-2-pyrrolidone which mix with a manganic acid lithium, carbon powder, or a binder, and it uses, or is a solvent. Moreover, in the example, although ammonium polyphosphate was used, ammonium phosphate, the 3rd ammonium phosphate, ammonium dihydrogenphosphate, etc. were able to acquire the effectiveness same about other ammonium phosphate compounds and ammonium phosphate conjugated compounds.

[Translation done.]